



Short Communication

Fast pyrolysis product distribution of biopretreated corn stalk by methanogen


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HIGHLIGHTS

- Methanogen pretreatment changed remarkably pyrolysis product distribution in bio-oil.
- After biopretreatment, the phenols content increased from 42.25% to 79.32%.
- Methanogen pretreatment improved the pyrolysis selectivity of CS for 4-VP.
- Biopretreatment increased the 4-VP content from 28.6% to 60.9% in bio-oil.
- Effects of biopretreated time on pyrolysis product distribution were insignificant.

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ABSTRACT

After pretreated by methanogen for 5, 15 and 25 days, corn stalk (CS) were pyrolyzed at 250, 300, 350, 400, 450 and 500 °C by Py-GC/MS and product distribution in bio-oil was analyzed. Results indicated that methanogen pretreatment changed considerably the product distribution: the contents of sugar and phenols increased; the contents of linear carbonyls and furans decreased; the contents of linear ketones and linear acids changed slightly. Methanogen pretreatment improved significantly the pyrolysis selectivity of CS to phenols especially 4-VP. At 250 °C, the phenols content increased from 42.25% for untreated CS to 79.32% for biopretreated CS for 5 days; the 4-VP content increased from 28.6% to 60.9%. Increasing temperature was contributed to convert more lignin into 4-VP, but decreased its content in bio-oil due to more other chemicals formed. The effects of biopretreatment time on the chemicals contents were insignificant.

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1. Introduction

Pyrolysis is one of the most important thermo-chemical technologies to utilize biomass such as wood wastes and agricultural residues. Biomass was converted into bio-oil, bio-char and bio-gas by using pyrolysis technology. Compared to other reactors, fluidized bed reactor given the most potential in converting biomass into bio-oil due to rapid devolatilization, high heating rate (Amutio et al., 2013; Chang et al., 2013; Heidari et al., 2014). The bio-oil was not only used as an alternative to petroleum, but included some high-valuable chemicals such as 5-hydroxymethyl furfural (HMF) (Torri et al., 2010), levoglucosan (LG) (Dobele et al., 2005), levoglucosenone (LGO) (Shen et al., 2010) and 4-vinyl phenol (4-VP) (Qu et al., 2013). These had been given much attention in last decades.

The chemical components of biomass are very complex, which result in a complex mixture of crude bio-oil, including hundreds of organic compounds and most of them in low contents. So it was difficult to obtain pure chemicals from bio-oil. To improve the pyrolysis selectivity of biomass to specific chemicals, some methods such as pretreatment and catalytic pyrolysis had been developed. The results of catalytic pyrolysis indicated that HZSM-5 increased the yield of aromatic hydrocarbons from 0.9 wt.% to 25.8 wt.% (Suchithra et al., 2012); zeolites has more selectivity of alcohols and phenols than alkaline catalysts (Leng et al., 2013; Wang et al., 2010); ZnCl₂ can maximize the furfural yield in pyrolysis (Lu et al., 2011).

In our previous study, corn stalk (CS) was pretreated by methanogen and then pyrolysis behaviors were analyzed by thermogravimetric analysis (TGA) and pyrolysis–gas chromatograph/mass spectrometry (Py-GC/MS) analysis (Wang et al., 2014). The results indicated that compared with untreated CS, the 4-VP content in bio-oil increased remarkably from 6.83% to 13.63% at

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500 °C. On the other hand, methanogen pretreatment improved the pyrolysis selectivity of CS. However, up to now, the pyrolysis product distribution of CS pretreated by methanogen with temperature is still unknown. So, in this paper, biopretreated CS like the literature (Wang et al., 2014) as feedstock was pyrolyzed at 250 to 500 °C by the Py-GC/MS and then product distribution in bio-oil was evaluated.

2. Methods

2.1. Methanogen pretreatment of CS

CS and biopretreatment method were the same with our previous study (Wang et al., 2014). The CS (1–2 cm in diameter) and the concentrate (including methanogen from fermentation of a Tianjin cattle manure) were sealed a reactor (1800 ML) and fermented for 5, 15 and 25 days, respectively. Methane produced during the fermentation was removed timely by an air pump. The fermentation conditions were: total solid (TS) 12%, fermentation temperature 38 °C and C/N 25:1. After fermentation, the samples were dried directly and stored in a bag. The chemical composition analyses of the samples were analyzed according to ASTM E1758-01.

2.2. Py-GC/MS analysis

The fast pyrolysis tests were conducted with a CDS Pyroprobe 5200HP pyrolyser (Chemical Data Systems) connected with a GC/MS (Perkin Elmer, Clarus 560) like the literature (Wang et al., 2014). In experiment, 0.3 mg sample was filled in a pyrolysis tube and then pyrolyzed at 250, 300, 350, 400, 450, and 500 °C respectively for 20 s with a heating rate of 20 °C/ms. The volatile products were analyzed online by GC/MS. The temperatures of transfer line and injector were kept at 280 °C. A TR-35MS capillary column (30 m * 0.25 mm i.d., 0.25 µm film thickness) was used to separate the volatile products. As carrier gas, helium (99.999%) was with a flow rate of 1 mL/min and a split ratio of 1:80. During analysis, the GC oven was heated from 40 to 180 °C with a heating rate of

10 °C/min for 2 min, and then to 280 °C with a heating rate of 15 °C/min for 2 min. The MS including a MCP detector was operated in EI mode at 70eV and the GC/MS interface was held at 280 °C. The NIST library and other literatures were used to identify the pyrolytic products.

3. Results and discussions

3.1. Effects of biopretreatment time and pyrolysis temperature on product distribution

By GC/MS analysis, all the identified chemical compounds were classified into six groups, including sugar (LG, LGO, etc.), linear carbonyls (hydroxyacetaldehyde, HAA; 1-hydroxy-2-propanone, HA, etc.), linear acids (acetic acid, AA; (acetyloxy) – acetic acid, etc.), linear ketones (2-propanone, 1-hydroxy, etc.), phenols (phenol, 4-VP, etc.), furans (furfural, FF; HMF, etc.). At 250 °C, sugar, linear carbonyls, linear acids, linear ketones were not produced in bio-oil from all samples; furans content was 27.23% from the untreated CS and was zero from biopretreated CS (Fig. 1). With an increase of pyrolysis temperature, sugar content, linear carbonyls content, linear ketones content increased firstly and then decreased in the bio-oil from untreated CS; linear acids and phenols contents decreased respectively. After biopretreatment, sugar content (at low 450 °C) and phenols content increased; linear carbonyls content and furans content decreased; linear acids content decreased firstly and then increased; linear ketones content showed different change trend depending on the pretreatment time. Linear ketones content increased with an increase of pyrolysis temperature from the pretreated CS for 5 days; however, it increased firstly and then decreased from the pretreated CS for 15 days and 25 days, and the decrease was observed when the pyrolysis temperature was over 450 °C. The effects of biopretreatment time on the six group chemicals contents were insignificant. From Fig. 1, phenols were the major component in bio-oil at every pyrolysis temperature. Phenols content from untreated CS was 42.25% and that was 79.32% from biopretreated CS for 5 day at 250 °C. Biopretreatment

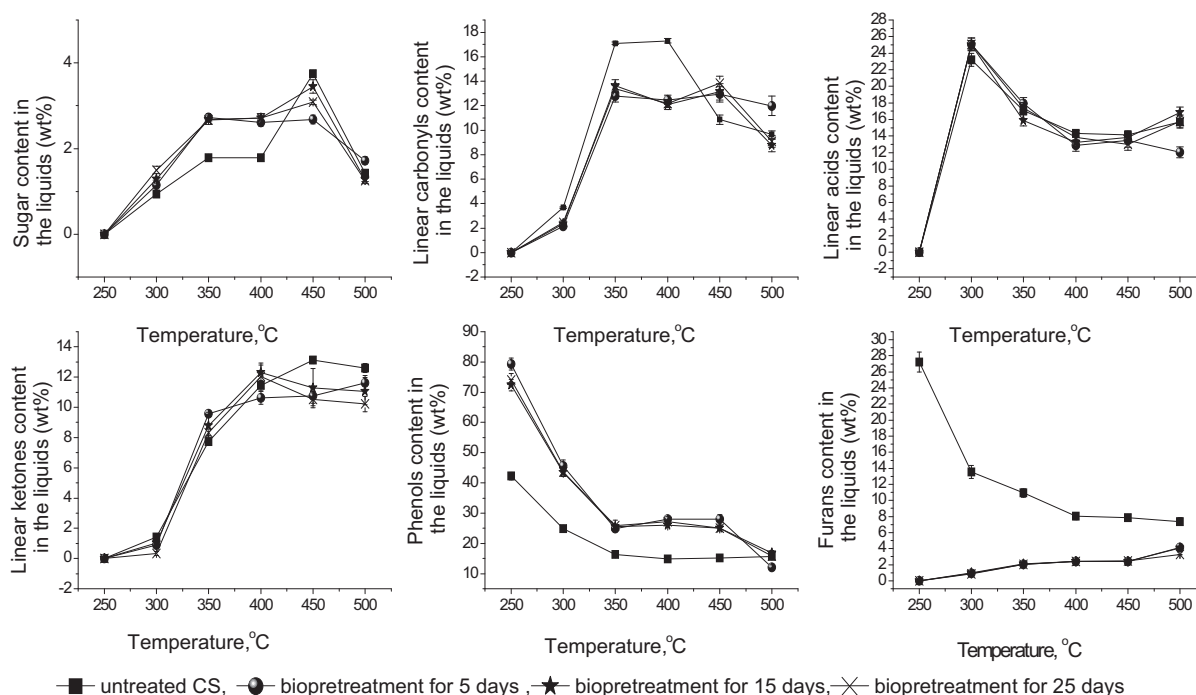


Fig. 1. Effects of pyrolysis temperature and biopretreatment time on product distribution in bio-oil from CS fast pyrolysis.

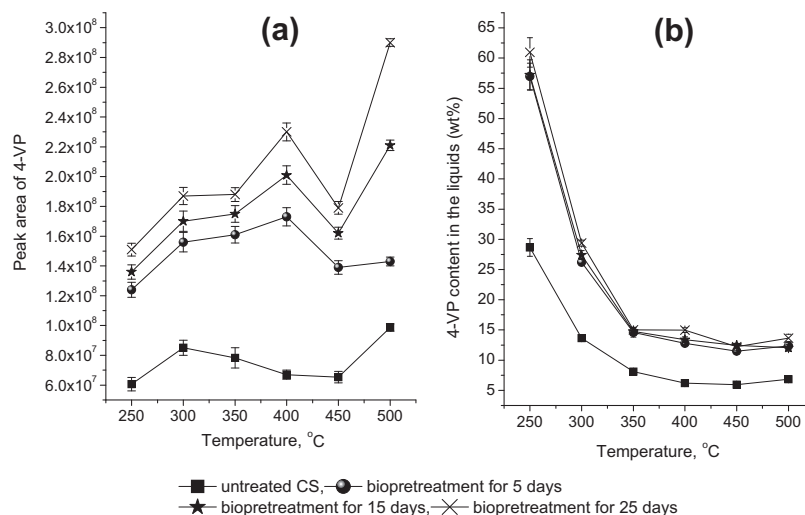


Fig. 2. Effects of pyrolysis temperature and biopretreatment time on the yield and content in bio-oil of 4-VP.

improved significantly the pyrolysis selectivity of CS to phenols especially at 250 °C.

In bio-oil, sugar are from the pyrolysis of cellulose (Shen et al., 2010), linear carbonyls, linear ketones and linear acids are from the pyrolysis of cellulose and hemicellulose (Dong et al., 2012; Shen and Gu, 2009); phenols are from the pyrolysis of lignin; furans are from the pyrolysis of hemicellulose, cellulose and extractive compounds (Lu et al., 2011; Wu et al., 2003). The degraded temperature of extractive compounds, hemicellulose, cellulose and lignin are at a range of 160–230 °C, 230–280 °C, 280–400 °C and 200–400 °C, respectively (Wang et al., 2014). During the biodegradation, extractive compounds (fructose, etc.) were degraded firstly. So at 250 °C, it was main the lignin pyrolyzed in feedstock, which resulted in the most content of phenols in bio-oil. With an increase of temperature, hemicellulose and cellulose were also degraded largely to form more compounds, which resulted in the decrease of phenols content and the increase of other chemicals content.

3.2. Effects of biopretreatment time and pyrolysis temperature on 4-VP

4-VP is a high-valuable and important chemical and is widely used in applications such as food, printing ink, rubber and medicine. Its content is the most in the phenols (Fig. 2b). Due to not allowing product collection, the exact 4-VP yield cannot be obtained by Py-GC/MS experiment. However, its yield changes could be estimated through a comparison of the total chromatographic peak area (Fig. 2a). With an increase of pyrolysis temperature, more lignin was degraded and the 4-VP yield increased. This indicated that high pyrolysis temperature is advantage to convert lignin into 4-VP. With an increase of biopretreatment time from 5 to 25 days, the 4-VP yield increased. But the effects of biopretreatment time on the 4-VP yield were limit. After biopretreated for 5 days, the 4-VP yield increased from 6.0×10^7 to 1.2×10^8 . However, it was only 1.5×10^8 from the CS pretreated for 25 days.

Hemicellulose, cellulose and lignin all are the three main components of biomass. The hemicellulose and cellulose are carbohydrate component and lignin is non-carbohydrate component. Comprising a complex and three-dimensional structure, lignin surrounds closed the hemicelluloses and the cellulose. Combining with other chemical components, a remarkable complex structure is formed in biomass cell wall. Extractive compounds, hemicellulose and cellulose are biodegraded easier by methanogen, but lignin is difficult. With an increase of biodegradation time, more and more extractive compounds, hemicellulose and cellulose were

degraded, which resulted in an increase of lignin content (Wang et al., 2014), and the lignocellulose structure of CS was destructed, which resulted in more lignin exposed. So, lignin was degraded easier and more 4-VP was produced, which could be the main reason that the 4-VP content increased from 28.6% for untreated CS to 60.9% (Fig. 2b) for biopretreated CS for 5 days. However, with an increase of pyrolysis temperature, hemicellulose and cellulose started to degrade largely into sugar, linear carbonyls, linear acids, linear ketones, furans and other chemicals. This was the main reason of a decrease of 4-VP content with an increase of pyrolysis temperature (Fig. 2b), although the 4-VP yield increased.

4. Conclusions

Methanogen pretreatment changed considerably the product distribution in CS pyrolysis bio-oil. After biopretreatment, the contents of sugar and phenols increased; that of linear carbonyls and furans decreased; the contents of linear ketones and linear acids changed slightly. The effects of biopretreatment time on the chemicals contents were insignificant. Methanogen pretreatment improved the pyrolysis selectivity of CS to phenols especially 4-VP. At 250 °C, the phenols content increased from 42.25% for untreated CS to 79.32% for CS biopretreated for 5 days; the 4-VP content increased from 28.6% to 60.9%. Increasing temperature enhanced the 4-VP yield, but decreased its content in bio-oil.

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References

- Amutio, M., Lopez, G., Alvarez, J., Moreira, R., Duarte, G., Nunes, J., Olazar, M., Bilbao, J., 2013. Flash pyrolysis of forestry residues from the Portuguese Central Inland Region within the framework of the BioREFINA-Ter project. *Bioresour. Technol.* 129, 512–518.
- Chang, S., Zhao, Z., Zheng, A., Li, X., Wang, X., Huang, Z., He, F., Li, H., 2013. Effect of hydrothermal pretreatment on properties of bio-oil produced from fast pyrolysis of eucalyptus wood in a fluidized bed reactor. *Bioresour. Technol.* 138, 321–328.

- Dobele, G., Rossinskaja, G., Dizhbite, T., Telysheva, G., Meier, D., Faix, O., 2005. Application of catalysts for obtaining 1,6-anhydrosaccharides from cellulose and wood by fast pyrolysis. *J. Anal. Appl. Pyrol.* 74, 401–405.
- Dong, C., Zhang, Z., Lu, Q., Yang, Y., 2012. Characteristics and mechanism study of analytical fast pyrolysis of poplar wood. *Energy Convers. Manage.* 57, 49–59.
- Heidari, A., Stahl, R., Younesi, H., Rashidi, A., Troeger, N., Ghoreyshi, A.A., 2014. Effect of process conditions on product yield and composition of fast pyrolysis of *Eucalyptus grandis* in fluidized bed reactor. *J. Ind. Eng. Chem.* 20, 2594–2602.
- Leng, S., Wang, X.D., Cai, Q.X., Ma, F.Y., Liu, Y.E., Wang, J.G., 2013. Selective production of chemicals from biomass pyrolysis over metal chlorides supported on zeolite. *Bioresour. Technol.* 149, 341–345.
- Lu, Q., Dong, C., Zhang, X., Tian, H., Yang, Y., Zhu, X., 2011. Selective fast pyrolysis of biomass impregnated with ZnCl_2 to produce furfural: analytical Py–GC/MS study. *J. Anal. Appl. Pyrol.* 90, 204–212.
- Qu, Y.C., Wang, Z., Lu, Q., Zhang, Y., 2013. Selective production of 4-vinylphenol by fast pyrolysis of herbaceous biomass. *Ind. Eng. Chem. Res.* 52, 12771–12776.
- Shen, D., Gu, S., 2009. The mechanism for thermal decomposition of cellulose and its main products. *Bioresour. Technol.* 100, 6496–6504.
- Shen, D.K., Gu, S., Bridgwater, A.V., 2010. Study on the pyrolytic behavior of xylan-based hemicellulose using TG–FTIR and Py–GC–FTIR. *J. Anal. Appl. Pyrol.* 87, 199–206.
- Suchithra, T.G., Sushil, A., Shyamsundar, A.C., Ram, B.G., 2012. Catalytic pyrolysis of green algae for hydrocarbon production using $\text{H}^+\text{ZSM-5}$ catalyst. *Bioresour. Technol.* 118, 150–157.
- Torri, C., Adamiano, A., Fabbri, D., Lindfors, C., Monti, A., Oasmaa, A., 2010. Comparative analysis of pyrolysate from herbaceous and woody energy crops by Py–GC with atomic emission and mass spectrometric detection. *J. Anal. Appl. Pyrol.* 88, 175–180.
- Wang, D.H., Xiao, R., Zhang, H., He, G., 2010. Comparison of catalytic pyrolysis of biomass with MCM-41 and CaO catalysts by using TGA–FTIR analysis. *J. Anal. Appl. Pyrol.* 89, 171–177.
- Wang, T., Ye, X., Yin, J., Lu, Q., Zheng, Z., Dong, C., 2014. Effects of biopretreatment on pyrolysis behaviors of corn stalk by methanogen. *Bioresour. Technol.* 164, 416–419.
- Wu, C., Chang, C., Tseng, C., Lin, J., 2003. Pyrolysis product distribution of waste newspaper in MSW. *J. Anal. Appl. Pyrol.* 67, 41–53.